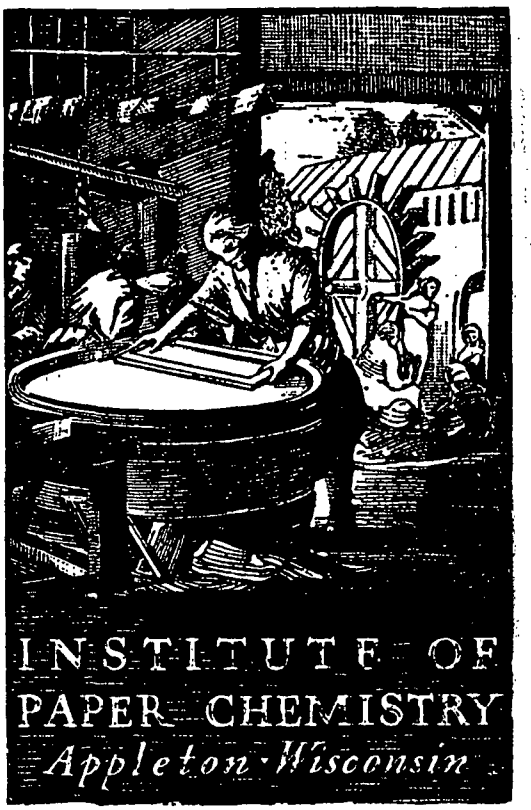

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STUDIES ON THE FACTORS GOVERNING RETENTION AND EFFECTIVENESS OF STARCH XANTHATES AND XANTHIDES BY WOOD PULP IN PAPERMAKING

Project 2580

Report Two

A Quarterly Report

to

AGRICULTURAL RESEARCH SERVICE
UNITED STATES DEPARTMENT OF AGRICULTURE

March 17, 1966

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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SUMMARY

This is the second quarterly report for Project 2580 undertaken in cooperation with Agricultural Research Service. The conversion of starch xanthate to starch xanthide appears to be involved in the critical step of the chain of events leading to the retention of starch xanthide by wood fibers. Absorption of the xanthate form is not a significant factor. This report describes exploratory investigations into the stoichiometry and pH dependency to increase our own understanding of the xanthate to xanthide conversion.

INTRODUCTION

This project was established with the Agricultural Research Service, United States Department of Agriculture to obtain the basic information that discloses the mechanisms governing the absorption of starch xanthate and starch xanthide by wood fibers used in papermaking. We are presenting the second quarterly report of the work undertaken to achieve this goal in accordance with the terms of the contract.

The preliminary experiment described in Report One established that starch xanthate is not absorbed by bleached, fines-free, softwood kraft fibers during contact times including up to one hour. At the time that report was presented, the analytical data for the highest fiber constency (1.0%) had not been completed. These data are now available and show no retention of starch xanthate, either with or without alum or at acidic or basic pH values.

These results are not too surprising in view of the experience in the Cereal Products Laboratory of the Northern Utilization Research and Development Division. However, these workers do report starch xanthate absorption on unbleached kraft fibers in the presence of alum (1).

The absence of xanthate sorption simplifies the retention study and allows us to concentrate on the factors involved in oxidizing starch xanthate to xanthide and its absorption on the fibers. The work reported here was undertaken in order to become acquainted with the conversion of starch xanthate to starch xanthide. It is our aim to isolate the critical rate-controlling step so that rate studies of xanthide sorption can lead to deductions concerning the retention mechanisms.

EXPERIMENTAL

STARCH XANTHATE

The material used for this report came from Ko-Kneader Runs No. 414 and 415. It was provided by the cooperator along with the following information:

Run No.	414	415
Starch g./100 g.	10.1%	9.96%
Starch xanthate g./100 g.	10.8%	10.74%
D.S. (meq. xanthate/meq. anhydroglucose unit)	0.114	0.122
Mole reactants/mole anhydroglucose unit:		
NaOH	0.508	0.494
CS_2	0.157	0.155

SODIUM HYPOCHLORITE

A proprietary product, Hilex, containing 5.25% sodium hypochlorite was used in this work. The stated concentration equals 0.704 molar sodium hypochlorite.

ELECTROMETRIC TITRATION

A model N Beckman pH meter was used with the model 41263 glass electrode. The meter was standardized against pH 10 and pH 7 buffers at room temperature. The 1.000N sulfuric acid or Hilex was mixed into the sample by a magnetic stirrer operating at a speed just sufficient to form a vortex "dimple" about a quarter of an inch deep. No provision was made to prevent the escape of gaseous products during the titrations.

REACTION OF STARCH XANTHATE WITH SODIUM HYPOCHLORITE

A sample of starch xanthate was neutralized to pH 5.5 and titrated with sodium hypochlorite in the presence of potassium iodide until the persistence of the blue starch iodine complex indicated the presence of an excess. This quantity of hypochlorite was the basis for subsequent experiments.

When 60 and 100% of the hypochlorite required for the blue end point at pH 5.5 were added to 10% xanthate solutions no blue color appeared at the high pH or after acidification. More hypochlorite was required at acidic pH values for the end-point reaction. It was almost as if the first addition of hypochlorite had disappeared. The amount of sulfuric acid required for acidification to pH 5.5 was a little less than would have been required if no oxidation had been attempted. This is reasonable only if hypochlorite is consumed in some way at the high pH levels.

The end-point reaction was obtained at high pH (9 to 11) when 500% of the theoretical amount for xanthide formation was added slowly. This result agrees with the total amount of sulfur in the sample, including by-products, if it is assumed it all disproportionates to sulfide. Hypochlorite is used for total sulfur determinations with cellulose xanthate [(2) p. 998].

There was no odor of hydrogen sulfide during most of these titrations. Occasionally the odor associated with carbon disulfide was noticed.

These experiments are summarized in Table I.

TITRATION OF STARCH XANTHATE WITH SULFURIC ACID

Potentiometric titration of xanthate solutions with acid followed by back-titration with base is a means of estimating the degree of substitution of starch

TABLE I

TITRATION OF STARCH XANTHATE WITH SODIUM HYPOCHLORITE

Notebook Page No.	Ko-Kneader Run Number	Starch Xanthate Concn.,%	pH Before NaOCl	pH Range During NaOCl Addition	NaOCl Addition (%Theory for Xanthide)	NaOCl Addition To Blue End-Point	Percent Theoretical NaOCl Consumed: Xanthide	Percent Theoretical NaOCl Consumed: Total Sulfur
54	414	5	5.5	–	0	Fast	167	30
58	414	10	12.4	(12.4-12.2) (4.9-6.3)	(100%) Fast	Slow	247	45
61	414	10	12.4	(12.4-12.0) (4.3-6.3)	(170%) Fast	Slow	273	50
63	414	10	5.0	4.7-6.2	0	Slow	225	41
71	415	2	8.0	11-7	0	Slow	310	62
73	415	2	7.5	(10-9)(7-6)	(116%) Fast	Slow	230	46
75	415	2	5.2	(9-8) (9-8)	(115%) Fast	Slow	287[a]	57
76	415	2	10.6	11.0-8.7	0	Slow	500	99
82	415	2	6.2	(11-10) (5.-6.5)	(100%) Fast	Slow	198	39

[a]Contained 0.25% alum, coagulated at 172% theoretical OCl^-.

xanthate (3). Our interest in these experiments was not centered on this aspect of the procedure. It was hoped that the pH of the half-equivalence points could be related to the pKa of ionic species possibly involved in xanthide formations.

Forty to ninety grams of xanthate solutions were titrated with 1.000N H_2SO_4 at 19 to 25°C. The pH of the solution was found to vary with time after each addition of acid. Consequently, a schedule for reading pH was established.

The potentiometric titration curves usually displayed the double inflection shown in the description of the analytical procedure (3). However, when using small increments of acid and reading the pH just after, and one minute after adding the acid, a third equivalence point was detected at about pH 2.9.

The first equivalence point is believed to be due to strong bases, such as excess NaOH, and the second equivalence point to xanthation by-products (3). The third equivalence point at pH 2.9 we attribute to the xanthate groups. It probably represents the completion of the hydrolysis of these groups from the starch. In any event, 5.9 milliequivalents of acid were consumed between the second and third points. This can be compared with the 6.2 milliequivalents of xanthate calculated from the data provided with the sample (Ko-Kneader Run No. 415, four days old). A pKa of about 3.5 for starch dithiocarbonate groups can be estimated from the buffering effect observed between the equivalence points.

TITRATION OF HILEX WITH SULFURIC ACID

The sodium hypochlorite solution being used in this work (25.0 ml.) was titrated with 1.000N sulfuric acid at room temperature. An average of 2.0 milliequivalents of acid were required to reach the first inflection at pH 10.5 and 15.5 milliequivalents additional were required to produce the second inflection

at pH 5.1. The observed half equivalence pH is high for sodium hypochlorite and may reflect the presence of undetermined additives in a proprietary product.

ESTIMATION OF pKa

The pKa, or acid hydrolysis constant expressed in reciprocal logarithmic units, is relatively independent of concentration and corresponds approximately to the half-equivalence point in acid-base titrations. The estimates of pKa obtained by titrations are shown in Table II along with some values obtained from the literature.

TABLE II

ESTIMATED pKa VALUES AND CERTAIN PUBLISHED VALUES

Compound		pKa	95% Confidence Level[a]
By-products, xanthation		7.0	± 0.2
Starch xanthate		3.5	?
By-products, after Hilex		6.4	± 0.1
Hilex		7.5	± 0.1
HOCl		7.25	–
H_2CO_3	first	6.36	–
	second	10.25	–
H_2S	first	7.04	–
	second	14.92	–

[a] Based on range.

DISCUSSION

A reaction scheme is presented by Ingram and Toms [(4) p. 4336] which describes the decomposition of organic xanthates in the presence of base and trithiocarbonate ions to organic alcohol, carbonate ions, and sulfide ions. This scheme is not accepted by some authorities (5). However, we have found it useful in gaining an understanding of the system we are working with.

Our data suggest that the ionic species titrated in the by-products portion of the xanthate curve is sodium hydrogen sulfide rather than sodium trithiocarbonate, in agreement with Ingram and Toms (4) and the published pKa values.

Treatment of starch xanthate solution with hypochlorite above pH 7 apparently removes free hydrosulfide ions since the by-product pKa is lower in subsequent titration. The species titrated then is probably the bicarbonate ion. According to Ingram and Toms data (4), mixtures of sodium bicarbonate and sodium hydrogen sulfide give titration curves more like sodium hydrogen sulfide than like sodium bicarbonate. Consequently, we should not expect to detect both bicarbonate and acid sulfide ions in a mixture by acid titration.

If starch xanthide is formed at high pH, then more hypochlorite would be required than at pH 5.5 specified in the standard procedure for xanthide preparation (6). At higher pH, all the by-product sulfur is present mainly as sulfide or as potential sulfide by hydrolysis, whereas at low pH varying amounts are lost by the escape of gaseous hydrogen sulfide.

If xanthate is to be converted to xanthide, all of the xanthate must react or it will disproportionate to form carbon disulfide and subsequently trithiocarbonate and then sulfide ions. On the basis of the total carbon disulfide added to the

xanthation reaction and the amount of starch xanthate formed, 251% (Run 414) and 208% (Run 415) of hypochlorite needed on the basis of starch xanthate to xanthide reaction must be added to satisfy all the reactive species. This is based on the assumption that each xanthate equivalent will consume one equivalent of hypochlorite and each mole of carbon disulfide added, but not present as xanthate, will require four equivalents of hypochlorite.

Another factor to be considered is that, if sodium trithiocarbonate is titrated rapidly with dilute acid, carbon disulfide and hydrogen sulfide are formed instead of hydrogen sulfide and carbon dioxide (4). This will reduce the amount of hypochlorite required by trithiocarbonate sulfur to 20% of that at high pH. Thus, when starch xanthate is neutralized to pH 5.5 (6) before cross-linking, the rate of acidification can change the amount of hypochlorite consumed by affecting the decomposition of the by-products. It is conceivable that starch xanthate concentration could also have an affect by changing equilibrium positions by mass action.

The reactants in cross-linking at pH 5.5 may be deduced from pKa values associated with the constituents. Starch xanthate groups (pKa ca. 3.5) are probably about 97% ionized. The hypochlorite is probably present as hypochlorous acid (pKa 7.) and about 6% hypochlorite. Hydrogen sulfide (pKa 7.04) would be about 7% ionized to acid sulfide ion.

The question of why pH 5.5 has become established by practice (6) as the most desirable for cross-linking with hypochlorite is puzzling. Not that it has been chosen on the basis of experience but from the standpoint of what is involved to make it the most desirable. None of the expected ionic species has a significant buffering capacity in this range. Rather it is about half-way between the pH values where buffering could be expected. For this reason, acetic acid is specified in the procedure for xanthide preparation (6).

FUTURE WORK

We shall continue to develop our understanding of the conditions peculiar to xanthide formation by hypochlorite oxidation. This will be done to the extent that is consistent with the needs of the project.

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